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Optical and electrical properties of chemically grown ZnS quantum dots

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Abstract : In this paper successful preparation of highly nano dispersive and nano crystalline ZnS semiconductor quantum dots by chemical method in polyvinyl alcohol (PVA) has been reported The optical absorption studies were done for size quantization Photoluminescence was carried out to study the presence of surface states The sizes of the particle were estimated from XRD and TEM studies Further the current-voltage measurement confirmed the presence of surface states

Keywords : Quantum dots, surface states, photoluminescence, Schottky junction

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1. Introduction

The study of optical and electrical properties of nano crystals (quantum dots) have become the topic of both theoretical and experimental interest. It is known that nano crystalline semiconductors (a few nano) exhibit the quantum confinement effect [1–4] and possesses physical properties that are intermediate between those corresponding to the bulk solid and molecules. As a consequence of quantum confinement, the continuum states in the conduction and valence bands are broken down into discrete states with energy spacing relative to the band edge which is inversely proportional to the square of the particle size [1,5,6]. This results in widening of the band gap compared to the bulk. This is observed in optical absorption spectra.

Nano crystals of II-VI semiconductors can be prepared without much difficulty. Moreover almost all these II-VI semiconductors are direct band gap materials and allow manipulation of particles by controlling the stoichiometry [7,8]. The electronic states called surface states are created within band gap during sample preparation. These surface states influence the thermo luminescence and photoluminescence (PI). The sizes of the particles are obtained from X-ray diffraction (XRD) studies and from transmission electron microscope (TEM) studies.

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2. Preparation

The aqueous solution of 6 wt% of poly vinyl alcohol (PVA), 2 wt% of zinc chloride ($ZnCl_2$) and 2 wt% of sodium sulfide (Na_2S) were prepared and then PVA solution and $ZnCl_2$ solutions were mixed in the ratio of 2 : 1.The solution was then stirred at a constant stirring rate for 4 hours and Na_2S solution was dropped up to maximum absorbency and kept in a dark chamber for 12 hours. The film was deposited over glass substrate and dried. The particle sizes were controlled by varying the surface temperature and pH value.

3. Experimental and result

3.1. XRD and TEM studies :

From the XRD study (Figure 1) it is found that the peaks are broadening and their width become larger as the particle's size become smaller. By using Scherrer formula the particle sizes are estimated as 6.2 nm and 7.1 nm for two ZnS samples of different pH values

The TEM studies were carried out and it confirmed the sizes and shapes of the particles. The particle having higher pH value was found to be smaller in size. The Figures 2 and 3 show the images obtained from the TEM studies for the samples S1

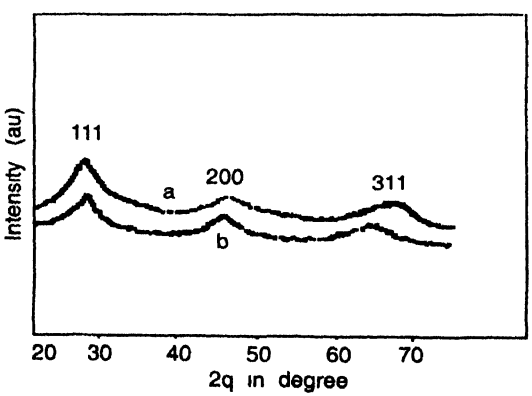

Figure 1. XRD peak (a) for S1,(b) for S2.

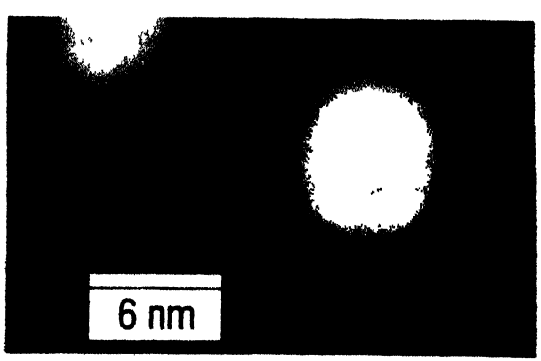

Figure 2. TEM image of ZnS quantum dot (S1).

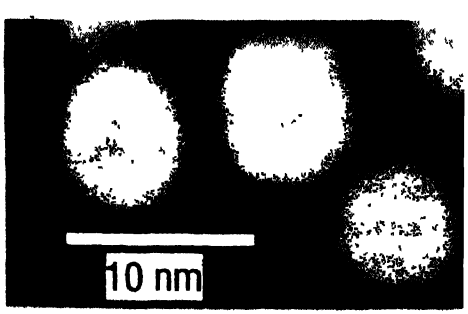

Figure 3. TEM image of ZnS quantum dot (S2).

and S2. Essentially isolated and spherical nano particles with in a size range 2–8 nm for S1 and 3–10 nm for S2 were observable and shown in the figure inset. The size distributions of the particles are shown in the inset of the images.

The Table 1 gives the comparison of the sizes of the particles obtained from the XRD for two samples S1 and S2 for different pH value and temperature.

Table 1. Comparison of the sizes of the particles.

pH value	Surface temp.	Size from XRD	Shape (TEM)
7	273°K	6.2 nm	Spherical
6.5	283°K	7.1 nm	Spherical

3.2. Optical absorption :

Optical absorption was studied at room temperature using UV/VIS spectrophotometer in the wavelength range 300–700 nm. Figure 4 shows the room temperature absorption of the different samples. The plot (c) for bulk ZnS gives the usual inter band absorption

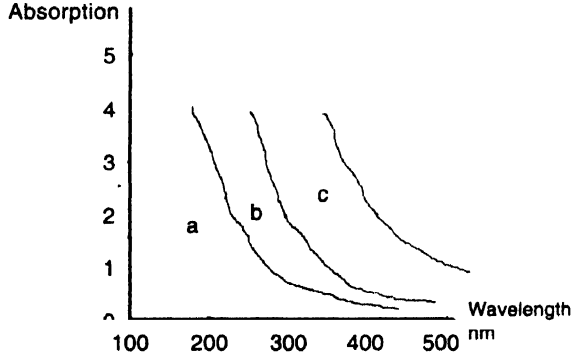

Figure 4. Absorption spectra of ZnS quantum dot and bulk ZnS (a) for S1, (b) for S2 and (c) for bulk.

spectrum. The plots (a) and (b) stand for the sample S1 (ZnS/PVA) at higher pH value for S2 (ZnS/PVA) at lower pH value respectively. Both the plots infer the strong blue shift of the particles (qd) with an absorption edge of 270 nm and 300 nm corresponding to an energy gap of 4.60 eV and 4.14 eV, respectively. The absorption edge for bulk ZnS occurs at 360 nm corresponding to a band gap of 3.45 eV. The increase in band gap of quantum dots by 1.15 eV and 0.688 eV for the samples with different sizes is significant. The strong blue shift obtained due to decrease in particle size establishes size quantization effect [4].

3.3. Photoluminescence :

The photoluminescence of ZnS quantum dots were recorded at room temperature when excited with 220 nm wavelength. The broad luminescence peaks called trapped luminescence arise from surface states. The luminescence peak is shifted towards higher energy for the particle of smaller size.

The transition appearance of P1 peaks (Figure 5) at energies lower than the band gap demonstrate that the luminescence are from surface states [9]. The density of surface states of nano particles would increase with decrease in particle size due to large surface to volume ratio. The presence of these surface states reduces the chance of excitonic emission *via* nonradiative surface recombination [10,11]. The band edge or excitonic emission thus overlaps with the absorption of the surface states which results photoluminescence at energies less than the band gap. The peak is shifted towards greater energy for the sample S1 having smaller size. The shift of the surface emission due to size variation has been reported earlier [10].

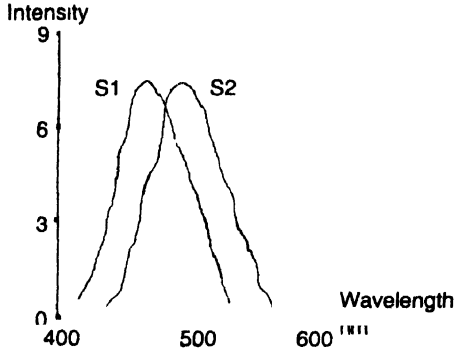

Figure 5. PL spectra of ZnS quantum dots (a) S1 and (b) S2

4. Electrical studies

The Schottky junction was fabricated by depositing Ag on ZnS quantum dots and forward biased current voltage (*I-V*) characteristics were studied using variable LCR meter. The plot for *I-V* characteristics for ZnS qd/Ag and for bulk ZnS/Ag are shown in Figure 6 and Figure 7 The rapid rise in current in qd/Ag at lower voltage than that in bulk/Ag suggests the presence of high density of surface states at the interface [12].

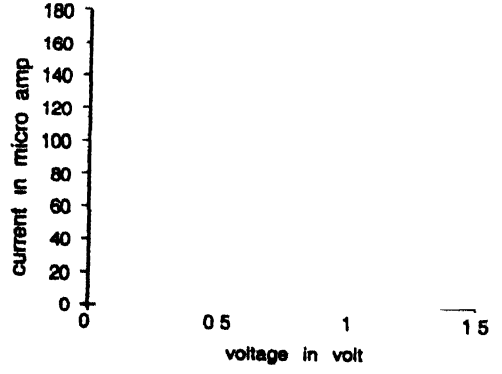

Figure 6. *I V* characteristics of ZnS quantum dot/Ag interface

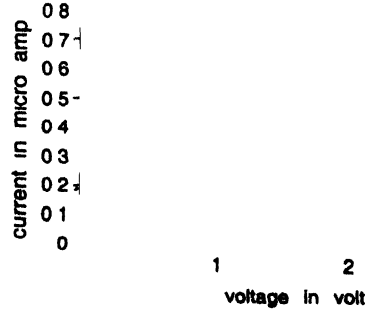

Figure 7. *I-V* characteristics of ZnS bulk/Ag interface

5. Conclusion

Significantly the narrow sized ZnS quantum dots were synthesized by non expensive chemical method. The particle size can easily be controlled by varying the reaction temperature and pH value. The PL studies of ZnS quantum dots have confirmed the presence of high density of surface states within the band gap. Further, the electrical study has confirmed the presence of the surface states in the interface.

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